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1.	Your reference	4981
2.	Patent application number *(The Patent Office will fill in this part)*	**9906731.6**
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	BG plc, 100 Thames Valley Park Drive, Reading, Berkshire, RG6 1PT, GB
	Patents ADP number *(if you know it)*	7166598001
	If the applicant is a corporate body, give the country/state of its incorporation	England & Wales
4.	Title of the invention	Formation, Processing, Transportation and Storage of Hydrates
5.	Name of your agent *(if you have one)*	William Illingworth-Law
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Intellectual Property Department BG plc, 100 Thames Valley Park Drive, Reading, Berkshire, RG6 1PT, GB
	Patents ADP number *(if you know it)*	7369762001
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number	Country / Priority application number *(if you know it)* / Date of filing *(day / month / year)*
7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application / Date of filing *(day / month / year)*
8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))*	yes

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Continuation sheets of this form	
Description	14
Claim(s)	8
Abstract	1
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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	1
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11. I/We request the grant of a patent on the basis of this application.

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12. Name and daytime telephone number of person to contact in the United Kingdom

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FORMATION, PROCESSING, TRANSPORTATION AND STORAGE OF HYDRATES

The present invention relates to economically advantageous methods of forming, processing, transporting and storing fluids, especially natural gas in the form of solid crystalline gas hydrates.

Applications include the transport of gas from fields where there is no existing local market or gas transport infrastructure and in exporting associated gas from offshore oilfields where there is no existing means of export or disposal. The technology eliminates the environmentally undesirable practice of flaring associated gas and gas released during well testing operations.

A gas hydrate is an ice-like crystal structure comprised mainly of water molecules during the formation of which gas molecules are incorporated in molecular scale cavities within the crystal structure. A unit volume of hydrate can contain in excess of 150 volumes of gas when the gas is at 20° C and atmospheric pressure.

Hydrates can be formed only by a limited range of compounds including methane, ethane, propane, butane, iso-butane, carbon dioxide, hydrogen sulphide, tetra-hydro furan and chlorofluorocarbons. The first six compounds named form the bulk of most natural gas fields.

Hydrate formation is strongly influenced by temperature and pressure. For natural hydrocarbon gases, hydrates will typically form at above 0° C (ice formation temperature) only at pressures above about 15 bar as shown in Figure 1. Hydrate formation in pipelines and equipment is thus a commonplace nuisance in offshore oil and gas fields, and expensive countermeasures are used to prevent them. Basic hydrate formation thermodynamics and properties are well understood and published, see e.g. Sloan E.D. "Clathrate Hydrates of Natural Gases" published by Marcel Dekker, New York 1990.

The ability to convert gas into a solid hydrate form is potentially useful for several purposes including storage or long distance transport because of the large amount of gas that hydrate can contain in a unit volume. Several processes have been proposed and patented for these purposes over many years, back to at least 1942, see for example US 5536893.

The detailed formation mechanisms of hydrates depends on whether the hydrate forming substance is, under the contacting conditions, a gas, a liquid non-miscible with water, or a miscible liquid. Most of the prior art patents are aimed at manufacture of hydrates from gas; in which case, production of hydrate occurs at the interfacial surface between gas and water, and the proposed production reactors are contacting devices which provide a large interface surface area to promote rapid formation. The engineering principles for several suitable contactor types are well known; most prior art patents cover the use of a single-stage spray (see for example US 2399723 and GB 568290) or bubbling pool ("bubble column", "sparged column") reactor (see for example US 3975167 and US 3514274). The latter type is frequently enhanced by the use of mechanical agitators.

Recent prior art (such as WO 97/26494) has looked at optimum arrangements of processing plants for the manufacture of gas hydrate.

Under the process conditions proposed by most prior art, the effluent from the reactor vessel will comprise a mixture of produced hydrate with a considerable amount of unreacted water in the form of a mixed slurry. This is a convenient form in which to continuously remove the hydrate product from the production reactor. However, the mixed slurry containing a considerable amount of unreacted water has a large volume and mass and so processing, transport and storage equipment must be correspondingly large to accommodate the slurry. All of the prior art, despite 50 years of study and proposals, has failed to produce an economically advantageous system for any of the intended applications. To the best of our knowledge, no commercial use has been achieved.

The applicant has carried out a programme of experiments studying the formation of a range of gas hydrates and their processing and has subsequently investigated the storage properties of these hydrates. From this work an innovative combination of technologies has been devised which together comprise an economic means for the manufacture, processing, transport and storage of gas hydrates in many of the applications described above.

According to a first aspect of the present invention, there is provided an apparatus for producing an essentially dry hydrate or concentrated hydrate slurry from a two phase mixture of hydrate and liquid or a three phase mixture of hydrate, liquid and gas, the apparatus comprising

a first separation device of a first fluid removing efficiency for receiving an input mixture of hydrate and liquid or hydrate, liquid and gas and for producing an intermediate mixture with a larger concentration of hydrate than the input mixture, and

a second separation device having a second higher fluid removing efficiency than that of the first separation service for receiving the intermediate mixture from the first separation device and for producing an essentially dry hydrate or concentrated hydrate slurry output.

A higher fluid removing efficiency relates to the ability of a device to produce a greater concentration of solids for the same input mixture.

The applicant has found that removing a proportion of the liquid and, if applicable, gas, from a two phase mixture of hydrate and liquid or a three phase mixture of hydrate, liquid and gas before supplying it to a generally more expensive but higher liquid removing efficiency second separation device such as a centrifuge significantly reduces the number and capacity of higher efficiency separating devices required whilst producing a greater quantity of the same quality output of essentially solid hydrate or concentrated slurry. This significantly

reduces costs and increases production levels making the use of hydrates more commercially attractive.

The provision of an apparatus having two separation devices of differing liquid removing efficiencies enables the production of essentially liquid free hydrate at reasonable cost. If one were to use one or more lower liquid removal efficiency separation devices the final product would still contain an excessive quantity of liquid. If one were to use a series of higher liquid removal efficiency separation devices such as centrifuges then the apparatus would be prohibitively expensive.

The applicant has found that an essentially solid or concentrated slurry final product form is especially useful for applications requiring stable handling of hydrate product at pressure substantially lower than the pressure required for hydrate production.

A device according to a second aspect of the present invention and which may be used as at least part of the first separation device of the first aspect of the present invention for separating gas from a three phase mixture of hydrate, liquid and gas comprises

a vessel with an inlet for receiving a three phase mixture of hydrate, liquid and gas;

the vessel having an internal surface against which the mixture is arranged to be directed such that the impact of the mixture against the surface disengages gas from the mixture and

the vessel having a chamber to collect mixture remaining after it has been directed against the internal surface, the chamber having an outlet and means to direct hydrate floating on liquid in the chamber to the outlet when in use.

The means to direct hydrate floating on liquid in the chamber to the outlet is preferably an upper boundary of the chamber, at least a portion of which is inclined to the horizontal when

in use with the outlet located at an upper portion of the chamber defined below the inclined portion of the upper boundary.

A device for separating gas, liquid and solid hydrate according to a third aspect of the present invention and as may be used as the first separation device of the first aspect of the present invention comprises

a vessel for receiving an input mixture of gas, liquid and hydrate;

a straining means mounted within the vessel and

means to direct an input mixture of gas, liquid and hydrate against the straining means such that gas is evolved to be collected or removed from the vessel, liquid passes through the straining means to be collected or removed from the vessel, and hydrate is collected by the straining means. The straining means may be for example a perforated screen or a woven mesh.

An essentially solid or concentrated slurry final product form which may be produced according to the first aspect of the present invention is preferably cooled before being stored or transported to enable it to remain stable for longer periods of time.

The cooling of a solid or concentrated slurry is difficult and expensive because of the poor heat transfer characteristics of such systems and the need to avoid the freezing of solids to the surfaces of a cooling device.

The inventors have solved this problem according to a further aspect of the present invention with a substantially dry hydrate cooling apparatus comprising

a container for receiving essentially solid or concentrated slurry hydrate;

a gas distribution device arranged to be supplied with fluidising gas when in use, the gas distribution device being arranged to be positioned in the container to pass fluidising gas through essentially solid or concentrated slurry hydrate in the container when in use to fluidise the hydrate and

means to provide cooling of the fluidised hydrate in the container.

The means to provide cooling to the fluidised hydrate is preferably the distribution device which is arranged to supply cooled fluidising gas. Alternatively or additionally the means to provide cooling to the hydrate may be means to supply an additional stream of cooled fluid through the fluidised hydrate to provide the cooling. This additional stream of cooled fluid may be passed through the fluidised hydrate in one or more conduits.

According to a still further aspect of the present invention there is provided a method for at least one of storage and transport of gas in the form of stable hydrate which is preferably used with hydrates prepared using one or more of the above aspects of the invention.

The invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 shows a typical natural gas hydrate equilibrium curve giving the pressure and temperature conditions required for formation of stable hydrate;

Figure 2 diagrammatically shows an apparatus according to the first aspect of the present invention for the production of an essentially solid or concentrated slurry of hydrate;

Figure 3 diagrammatically shows a sequence of steps in a process for forming hydrate incorporating the method according to the first aspect of the present invention;

Figures 4 to 7 show preferred devices for performing various steps in the process shown in Figure 3;

Figure 8 is a graph showing cumulative gas evolution from a sample of initially high gas content typical natural gas mixture hydrate; and

Figure 9 is a diagram showing the temperature of various regions of a mass of hydrate stored for 5 days in a ship's hold at ambient temperature and pressure.

Figure 2 diagrammatically shows a system according to the first aspect of the present invention for the two stage removal of fluid from a two phase mixture of hydrate and liquid or a three phase mixture of hydrate, liquid and gas. The mixture 1 is supplied to a first stage 3 of a water removal system 2. The first stage 3 may be any suitable separating device such as a hydrocyclone which is well known in the art or a device to mechanically remove hydrate floating on a liquid which may be liquid separated from the slurry as described later. The output 4 from the first stage 3 is fed to the second stage 5 which is a more efficient separating device than the first stage such as a centrifuge which produces a substantially dry hydrate product 6.

Figure 3 is an outline of a hydrate formation process tested using a pilot plant and laboratory experiments, the process incorporating the fluid removal system shown in Figure 2. A process reactor 10, for example as shown in our earlier international patent application published as WO97/26494, produces a hydrate/gas/liquid mixture 11. The mixture 11 is passed to device 12 described below which is arranged to separate the majority of the gas phase from the mixture 11. A separated substantially liquid and solid free gas stream 13 can be utilised by for example being returned to the process reactor 10 for the formation of further hydrate or by being delivered to a device for power generation or it may be burned. A substantially gas free liquid and solid slurry stream 14 is passed to a first separating device 15 forming the first stage 3 of the water removal system 2, an example of which is described later, which is arranged to produce a liquid stream 16 containing a low level of solids and a slurry stream 17 with a higher solid hydrate concentration than input stream 14. Stream 16 is passed back to the process reactor 10 to be used in the further production of hydrate. Alternatively separators 12 and 15 may be combined into a single device 30 described later.

Stream 17 is passed via an optional cooling device 18 to the second stage of the water removal system 2, comprising the more efficient separating device 5 than that of the first stage. In this example the separator of the second stage is a centrifuge. The inventors of the present invention have found that a continuous screening centrifuge 5 produces a 95% to 99.5% liquid free stream 19 in the form of a granular, flowable solid and a liquid stream 20 containing extremely low levels of solids which may be returned to the process reactor 10. Alternatively, the second more efficient liquid separating device could be a high pressure filtration device such as a tube-press. However, the centrifuge has been found by the inventors to be better suited to a large scale application.

Stream 19 may optionally be passed into device 21 where it is cooled either by direct contact with a gas stream 22 supplied in this case at high pressure and low temperature or indirectly by passing an additional stream of cooling medium 23 through conduits passing through the body and walls of the device. This latter option increases the process complexity but means that a smaller high pressure gas stream 22 is needed only to aid motion of the solids termed 'fluidisation' and improve heat transfer to the solids. The gas stream 22 may be either of hydrate forming or non-hydrate forming gases - in the former case an advantage is gained in that any moisture entering device 21 in stream 19 may be converted into additional hydrate.

The fluidising/cooling gas 22 and cooling medium 23 exit device 21 separately (streams 24 and 25). The dry cold solids stream exits device 21 and may be depressurised by device 26 to atmospheric conditions and loaded into a transportation or storage device 27.

Gas separating device 12 may be of the type as illustrated in Figure 4. An input stream 11 is arranged to enter the vessel 40 via inlet 41 and in this example is directed downwards by a suitably shaped portion 42 of the inlet. The gas present in the input mixture 11 is disengaged from the mixture by impacting the mixture against a suitable surface 43, in this case part of an insert 44. The generated gas exits the vessel as a gas stream 13 via outlet 45. The

surface 43 directs the remaining liquid and solids from the mixture into a downcomer 46 which is sized (by known methods) to ensure that particles of hydrate are entrained in the downward flow. The insert 44 is shaped to provide a space or chamber 47 at the base of the vessel 40 with an upper boundary 48 which is inclined or sloping relative to the horizontal when in use. An offtake 49 for a substantially gas free liquid and solid slurry stream 14 is located at the upper part of this space 47 and the inclined or sloping upper boundary 48 is arranged to direct hydrate floating on liquid in the space 47 to the offtake 49. This design avoids accumulation of hydrate within the device and subsequent blockage.

Either of two preferred devices can perform the function of separating device 15. One is a hydrocyclone - a device familiar to those skilled in the art of solid-liquid separation but normally used for the separation of solids from liquid of lower density than in the present invention.

Studies performed by the applicant have identified an alternative device 15 suitable for this application which involves separating solids from a liquid of higher density. This device is illustrated in Figure 5. Stream 14 enters a vessel 50 of the device 15 via an inlet 51 and is directed upwards by a suitable portion 52 of the inlet.

Liquid stream 16 is removed from the base of the vessel through outlet 53. The diameter of the vessel 50 is such that hydrate particles are not drawn down by the flow of liquid in stream 16 - instead the hydrate collects to form a floating mass 54 in the upper part of the vessel 50. The mass of hydrate 54 floats on the liquid contained in the vessel. The section of the mass of hydrate 54 which floats above the surface of the liquid becomes drained of liquid by gravity. A scraping device 55 positioned at the top of the vessel 50 scrapes hydrate off the top of the floating mass 54 to an outlet 56 to form stream 17.

Device 30 which may be used as an alternative to the combination of devices 12 and 15 is illustrated in Figure 6. It comprises a straining means, in this case a perforated screen 60

mounted within a pressure vessel 61. Stream 11 enters the vessel through inlet 62 and is directed downwards by a suitable distribution device 63 which may be a suitably directed portion of the inlet 62.

A gas stream 13 is generated by the impact of the input hydrate/liquid/gas mixture onto the screen 60 and the generated gas stream 13 exits from the top of the vessel 61 through a gas outlet 64. Liquid and hydrate which impinge against the screen 60 travel down it under the influence of gravity in the direction illustrated. During this passage, liquid passes through the perforations in the screen 60. The concentrated slurry (stream 17) is drawn from the vessel through outlet 65. The liquid 66 that passes through the screen 60 accumulates in the base of the vessel 61 and is drawn out of the vessel, as stream 16, through outlet 67. Laboratory tests at process conditions have found that such a device can concentrate a stream containing less than 5% by volume hydrate to one containing more than 30% by volume of hydrate.

The second more efficient stage 5 of the two stage water removal apparatus is in this example a centrifuge of the type commonly known as a continuous screening centrifuge and as is well known in the art. Laboratory work with a small pressurised centrifuge has shown that a full size centrifuge can produce a hydrate product which contains less than 2% by volume of water.

Device 21 is a fluidised bed in the present example. The applicant has found that the fluidisation of hydrate and ice particles is feasible at low temperatures and high pressures. In laboratory studies beds of hydrate and ice particles could be fluidised smoothly at a temperature of -10°C and below provided high pressure was maintained. Experiments were performed at -10°C to -70°C and at pressures of 3.5 to 28 bar. By comparison of the heat transfer rates from device 21 with those seen in conventional cooling devices for substantially solid streams we have found this to be the most economic method of adequately cooling the

hydrate product to a temperature suitable for transport. Figure 7 shows an arrangement of such a bed. The bed 70 is contained within a pressure vessel 71 suitable for the pressures and temperatures necessary for the process. The pressure vessel 71 is shaped with the bed 70 arranged to be located in a lower portion 72 of the vessel 71. The upper portion 73 of the vessel 71 is arranged to direct any fluidised particles leaving the lower portion 72 back to the lower portion. In the example illustrated in Figure 7, this is achieved by the provision of an inclined lip 74 around the upper periphery of the lower portion 72 to direct any particles leaving the bed 70 back to the lower portion of the vessel 71. This structure contains the bed 70 and avoids the carriage of smaller solid particles out of the top of the bed 70 (alternatively shaped internals may be used to provide the desired bed geometry in a pressure vessel of more conventional shape). Solids from separator 5 are added to the bed 70 via inlet 75 so that they fall down into the bed. Fluidising gas 22 is introduced through inlet 76 and thence via a distribution system 77 to the majority of the base of the bed. The fluidising gas 22 is preferably a hydrate forming gas so that any moisture entering the fluidised bed from stream 19 is converted into hydrate to maintain the hydrate virtually dry. The fluidising gas 22 may also provide cooling to the hydrate in the bed 70. The fluidising gas 22 exits the bed 70 and leaves the vessel 71 via outlet 78 after passing, optionally, through a conventional cyclone device 79 to remove small entrained particles of ice and hydrate. Alternatively or additionally cooling medium 23 from one or more external sources may be passed through the bed 70 either directly from the distribution system 77 using for example evaporative refrigerant or as illustrated in Figure 7 through conduits 80. As further solids are added to the bed 70 the level of the bed rises and solids overflow out of the bed 70 via chute 81 and outlet 82 maintaining the level of the bed 70 substantially constant. In some circumstances, e.g. a large installation, a bed may be subdivided by a series of substantially vertically orientated baffles 83 only one of which is shown in Figure 7, over which solids will flow from entry region(s) of relatively high temperature to exit regions of low temperature.

Depressuring device 26 shown diagrammatically in Figure 3 could be any of a range of known technologies for reducing the pressure of a solid stream. The applicant uses a lock

hopper system where batches of solids are introduced into pressurised vessels, the vessels are then isolated by means of valves and the vessels then depressurised with the exhaust gas optionally being initially routed to previously depressurised vessels to save on the costs of recompression.

Any means of transporting or storing a chilled bulk solid mass of hydrate may be used as convenient. Examples might be a container, the hold of a ship or a railway wagon. The transporting or storing means is preferably insulated.

The applicant has performed studies to determine the volume of gas evolved from a sample of relatively pure typical natural gas hydrate at various temperatures. The sample of relatively pure hydrate may be, but it is not necessarily, produced by the method and apparatus described above.

Figure 8 shows the volume (V) of gas evolved indicated on the right hand ordinate (Y-axis) and temperature (T) indicated on the left hand ordinate for a sample of hydrate formed from a typical natural gas mixture over a period of time (t) measured in hours on the abscissa (X-axis) at ambient pressure. As can be seen from Figure 8 a negligible amount of gas is evolved during storage of the natural gas hydrate at -60°C and -40°C. However when the temperature of the hydrate is increased to -37°C the hydrate is converted into ice and natural gas. This is because at ambient pressure and -60°C and -40°C natural gas hydrate is on or above the equilibrium curve in the stable region as shown in Figure 1. However, when the temperature is increased to -37°C at ambient pressure the hydrate crosses to the other side of the equilibrium curve in the unstable region and is converted into natural gas and ice. Thus the natural gas hydrate has been found to exist only in the stable region of its equilibrium curve where it releases only a negligible amount of its gas content whereas in an unstable region it releases substantially all of its gas content and is converted into ice and natural gas. Thus the hydrate described above is unable to exist above substantially -37°C at ambient pressure.

Therefore to transport or store a typical natural gas hydrate at ambient pressure the majority of the hydrate must be maintained at or below about -37°C for it to remain stable otherwise it will decompose into natural gas and ice. However to maintain a large volume of hydrate at such low temperatures for a suitable period of time, for example a few day or weeks, is considered prohibitively expensive.

It has also been found from economic studies that the gas content of any hydrate used for transportation or storage should preferably be of the order of 150 to 200 volumes of gas (for gas at atmospheric pressure and temperature) per volume of hydrate. If such a hydrate gas content is not achieved then such large ships or large numbers of small ships or containers will be required as to make the use of hydrates uneconomic when compared with other known alternatives for gas storage or transportation.

The applicant has surprisingly found that according to a still further aspect of the present invention storage or transport of hydrate with at least the majority of the hydrate remaining in a stable state for at least 24 hours can be performed by the provision of the hydrate in a mass without the need for external cooling.

Figure 9 shows the temperature profile of just such a mass of hydrate in a ship's hold with an initial storage temperature of -50°C after 5 days have elapsed. The ambient temperature at the top of the hold is 20°C and the ambient temperature at the bottom of the hold is 15°C. As can be seen only the edges of the original mass of hydrate fall below the stable temperature of approximately -37°C at atmospheric pressure and are converted into water (ice) and natural gas. The vast majority, in this case 95%, of the hydrate remains as stable hydrate with only 5% being converted into natural gas and water in the form of ice.

Although insulation of the mass of hydrate is not necessary its use is preferred in some circumstances as it will enhance the length of time that the hydrate remains stable. Insulation may be provided in whatever transport or storage device is being used such as the hold of a ship, container or railway wagon.

Since only the edges of a mass of hydrate are decomposed into ice and gas within a normal transport or storage period of a few days, as the size of the mass of hydrate is increased the proportion of hydrate that remains stable over the same period is increased. A preferred mass of hydrate for use in the present invention has a minimum dimension of 2m in any direction or a more preferred dimension of at least 10m in any direction. However, this of course depends upon the expected duration of the transportation or storage.

The hydrate used for the above method of storage and transport is preferably substantially pure to provide a commercially viable volume of gas in a suitably small volume of hydrate.

The hydrate used for the above method of storage and transport is preferably substantially dry or a concentrated slurry to reduce the proportion of non-gas carrying material to be stored or transported making the method of storage or transport of the present invention even more economically attractive.

Many modifications may be made to the examples described above without departing from the scope of the invention as defined in the following claims. For example any suitable separation devices may be used in the apparatus for producing an essentially solid hydrate or concentrated hydrate slurry from a hydrate, liquid and optionally gas mixture provided that the second device is of a higher liquid removing efficiency than the first.

CLAIMS

1. An apparatus for producing an essentially solid hydrate or concentrated hydrate slurry from a two phase mixture of hydrate and liquid or a three phase mixture of hydrate, liquid and gas, the apparatus comprising

a first separation device of a first fluid removing efficiency for receiving an input mixture of hydrate and liquid or hydrate, liquid and gas and for producing an intermediate mixture with a larger concentration of hydrate than the input mixture; and

a second separation device having a second higher fluid removing efficiency than that of the first separation device for receiving the intermediate mixture from the first separation device and for producing essentially solid hydrate or concentrated hydrate slurry output.

2. An apparatus according to claim 1, wherein the second separation device is a centrifuge.

3. An apparatus according to claim 1 or claim 2, wherein the first separation device comprises a vessel to receive an input mixture of hydrate and liquid, means to remove hydrate floating on top of the mixture and means to remove liquid from a lower portion of the vessel.

4. An apparatus according to claim 3, wherein the means to remove hydrate floating on top of the liquid is a scraper arranged to direct removed hydrate to an outlet.

5. An apparatus according to claim 1 or claim 2, wherein the first separation device is a hydrocyclone.

6. An apparatus according to claim 1 or claim 2, wherein the first separation device includes:

a vessel with an inlet for receiving a three phase mixture of hydrate, liquid and gas;

the vessel having an internal surface aginst which the mixture is arranged to be directed such that the impact of the mixture against the surface disengages gas from the mixture and

the vessel having a chamber to collect mixture remaining after it has been directed against the internal surface, the chamber having an outlet and means to direct hydrate floating on liquid in the chamber to the outlet when in use.

7. An apparatus according to claim 6, wherein the means to direct solid floating on liquid in the chamber to the outlet is an upper boundary of the chamber, at least a portion of which is inclined to the horizontal when in use with the outlet located at an upper portion of the chamber defined below the inclined portion of the upper boundary.

8. An apparatus according to claim 6 or claim 7, wherein the internal surface of the vessel against which the mixture is arranged to be directed is a surface above the chamber when in use and a downcomer is provided to direct mixture remaining after it has been directed against the surface to the chamber.

9. An apparatus according to claim 8, wherein the internal surface of the vessel is shaped to direct mixture remaining after it has been directed against the internal surface to the downcomer under gravity when in use.

10. An apparatus according to claim 1 or claim 2, wherein the first separation device comprises:

a vessel for receiving an input mixture of gas, liquid and solid hydrate;

a straining means mounted within the vessel; and

means to direct an input mixture of gas, liquid and hydrate against the straining means such that gas is evolved to be collected or removed from an upper portion of the vessel, liquid passes through the straining means to be collected or removed from a lower portion of the vessel, and hydrate is collected by the straining means.

11. An apparatus according to claim 10, wherein the straining means is a perforated screen arranged such that hydrate collected by the screen travels down the screen to be collected or removed from the vessel.

12. An apparatus according to claim 11, wherein the screen is curved and the means to direct the mixture against the screen is arranged to direct the mixture down against the screen such that hydrate collected by the screen slides off the screen with a component of its motion in an arc.

13. An apparatus according to any of the preceding claims including a hydrate cooling apparatus for cooling an essentially dry hydrate or concentrated slurry output produced by the second separation device, the hydrate cooling device comprising:

a container for receiving essentially solid or concentrated slurry hydrate;

a gas distribution device arranged to be supplied with fluidising gas when in use, the gas distribution device being arranged to be positioned in the container to pass fluidising gas through essentially dry hydrate or concentrated slurry hydrate in the container when in use to fluidise the hydrate; and

means to provide the passage of a cooling medium through fluidised hydrate in the container when in use.

14. An apparatus according to claim 13, wherein the means to provide the passage of a cooling medium through fluidised hydrate in the container is the gas distribution device which is arranged to supply cooled fluidising gas.

15. An apparatus according to claim 13 or claim 14, wherein the means to provide the passage of a cooling medium through fluidised hydrate is a means to supply a stream of cooling fluid, separate from the fluidising gas, through the fluidised hydrate.

16. An apparatus according to any of claims 13 to 15, wherein the gas distribution device is arranged to be supplied with hydrate forming fluidising gas.

17. An apparatus for producing an essentially solid hydrate or concentrated hydrate slurry substantially as hereinbefore described with reference to the accompanying drawings.

18. A method of storing or transporting hydrate produced by the apparatus according to any of the preceding claims comprising providing the hydrate in a stable form.

19. A method according to claim 18, wherein the hydrate is essentially dry hydrate or concentrated slurry hydrate.

20. A method according to claim 18 or claim 19, wherein the hydrate is provided in an insulated container.

21. A method according to any of claims 18 to 20, wherein the hydrate is provided in a bulk mass having a minimum dimension of 2 metres in any direction.

22. A method of storing or transporting hydrate substantially as hereinbefore described

with reference to the accompanying drawings.

23. A device for separating gas from a three phase mixture of hydrate, liquid and gas, the device comprising

a vessel with an inlet for receiving a three phase mixture of hydrate, liquid and gas;

the vessel having an internal surface against which the mixture is arranged to be directed such that the impact of the mixture against the surface disengages gas from the mixture and

the vessel having a chamber to collect mixture remaining after it has been directed against the internal surface, the chamber having an outlet and means to direct hydrate floating on liquid in the chamber to the outlet when in use.

24. A device according to claim 23, wherein the means to direct solid floating on liquid in the chamber to the outlet is an upper boundary of the chamber, at least a portion of which is inclined to the horizontal when in use with the outlet located at an upper portion of the chamber defined below the inclined portion of the upper boundary.

25. A device according to claim 23 or claim 24, wherein the internal surface of the vessel against which the mixture is arranged to be directed is a surface above the chamber when in use and a downcomer is provided to direct mixture remaining after it has been directed against the surface to the chamber.

26. A device according to claim 25, wherein the internal surface of the vessel is shaped to direct mixture remaining after it has been directed against the internal surface to the downcomer under gravity when in use.

27. A device according to claim 26, wherein the internal surface of the vessel presents a substantially conical or frusto-conical surface with the conical or frusto-conical axis

arranged substantially vertically when in use and the narrower part of the cone or frusto-cone arranged below the wider part.

28. A device according to any of claims 23 to 27, wherein the vessel has an outlet for gas disengaged from the mixture to exit the vessel.

29. A device for separating gas from a three phase mixture of hydrade, liquid and gas substantially as hereinbefore described with reference to figure 4 of the accompanying drawings.

30. An apparatus for separating gas, liquid and hydrate comprising:

a vessel for receiving an input mixture of gas, liquid and hydrate;

straining means mounted within the vessel: and

means to direct an input mixture of gas, liquid and hydrate against the straining means such that gas is evolved to be collected or removed from the vessel, liquid passes through the straining means to be collected or removed from the vessel, and hydrate is collected by the straining means.

31. An apparatus according to claim 30, wherein the straining means is a perforated screen arranged such that hydrate collected by the screen travels down the screen to be collected or removed from the vessel.

32. An apparatus according to claim 31, wherein the screen is curved and the means to direct the mixture against the screen is arranged to direct the mixture down against the screen such that hydrate collected by the screen slides off the screen with a component of its motion in an arc.

33. An apparatus for separating gas, liquid and solid hydrate substantially as hereinbefore described with reference to figure 6 of the accompanying drawings.

34. A hydrate cooling apparatus comprising:

a container for receiving essentially dry or concentrated slurry hydrate;

a gas distribution device arranged to be supplied with fluidising gas when in use, the gas distribution device being arranged to be positioned in the container to pass fluidising gas through essentially dry or concentrated slurry hydrate in the container when in use to fluidise the hydrate; and

means to provide the passage of a cooling medium through fluidised hydrate in the container when in use.

35. An apparatus according to claim 34, wherein the means to provide the passage of a cooling medium through fluidised hydrate in the container is the gas distribution device which is arranged to supply cooled fluidising gas.

36. An apparatus according to claim 34 or claim 35, wherein the means to provide the passage of a cooling medium through fluidised hydrate is a means to supply a stream of cooling fluid, separate from the fluidising gas, through the fluidised hydrate.

37. An apparatus according to any of claims 34 to 36, wherein the gas distribution device is arranged to be supplied with hydrate forming gas.

38. A hydrate cooling apparatus substantially as hereinbefore described with reference to figure 7 of the accompanying drawings.

39. A method for at least one of storing or transporting hydrate, wherein substantially all

of the hydrate is in stable form.

40. A method according to claim 39, wherein the hydrate is essentially dry hydrate or concentrated slurry hydrate.

41. A method according to claim 39 or claim 40, comprising providing the hydrate in a bulk mass.

42. A method according to claim 41, wherein the bulk mass of hydrate is provided in an insulated container.

43. A method according to claim 41 or claim 42, wherein the bulk mass of hydrate has a minimum dimension of 2 metres in any direction.

44. A method according to claim 43, wherein the bulk mass of hydrate has a minimum dimension of 10 metres in any direction.

45. A method according to any of claims 39 to 44, wherein the hydrate is stored or transported at substantially ambient pressure.

46. A method according to any of claims 39 to 45, wherein the hydrate is stored or transported at substantially ambient temperature.

47. A method of storing or transporting hydrate substantially as hereinbefore described with reference to figure 9 of the accompanying drawings.

ABSTRACT

The present invention relates to economically advantageous methods of forming, processing, transporting and storing fluids, especially natural gas in the form of solid crystalline gas hydrates.

It has been found that a mixture of hydrate, liquid and optionally gas can be economically and effectively dried using a two stage drying process in which a more efficient, but generally more expensive, fluid removing efficiency separation service is used for the second stage.

A number of separation devices are also disclosed. A device for effectively and economically cooling substantially dry hydrate is also disclosed, as is a method for economically storing and transporting hydrate.

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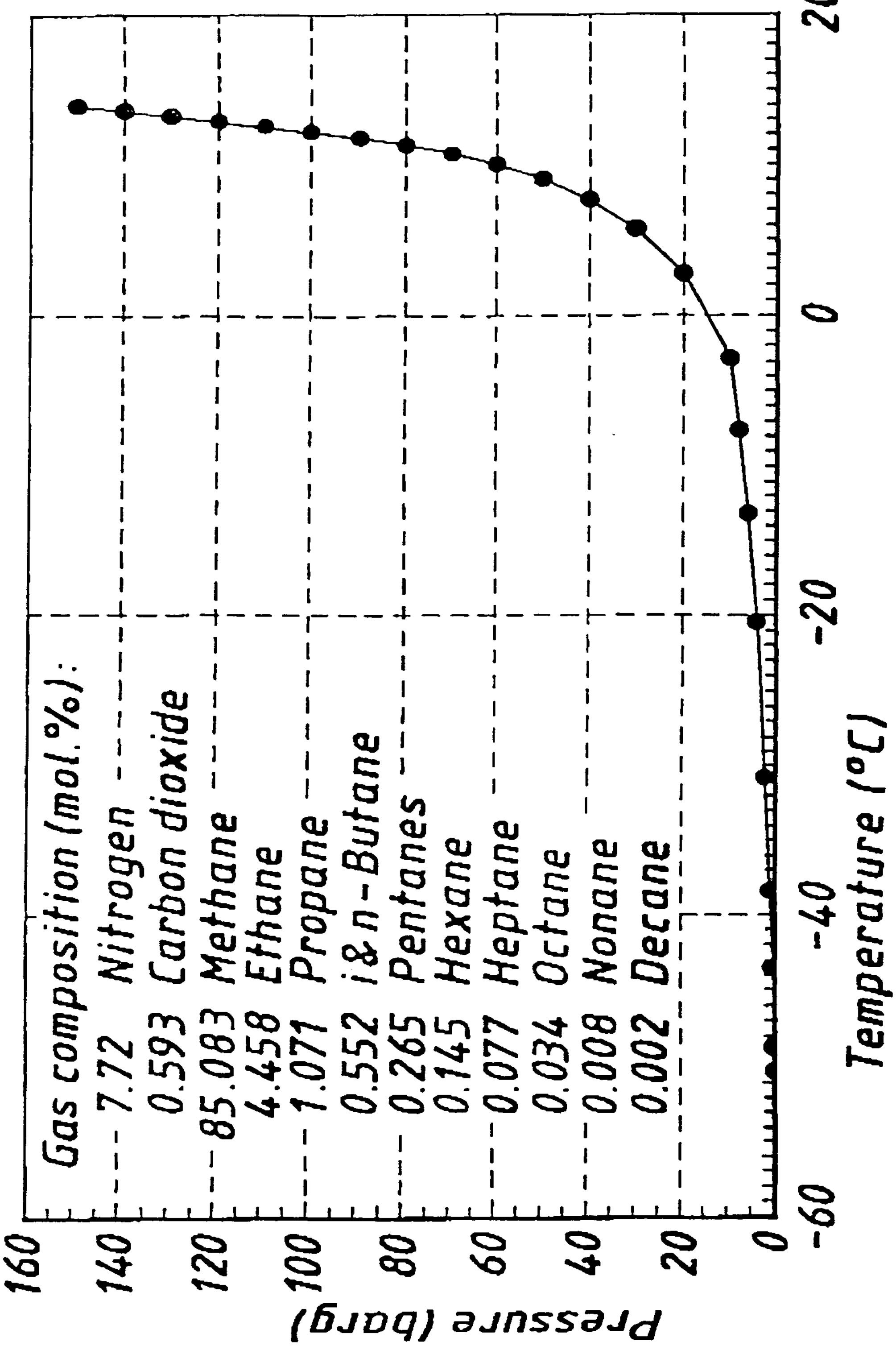
FIG.1.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85.083 Methane
4.458 Ethane
1.071 Propane
0.552 i & n-Butane
0.265 Pentanes
0.145 Hexane
0.077 Heptane
0.034 Octane
0.008 Nonane
0.002 Decane
Pressure (barg)
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140
120
100
80
60
40
20
0
Temperature (°C)
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-40
-20
0
20

FIG. 2.

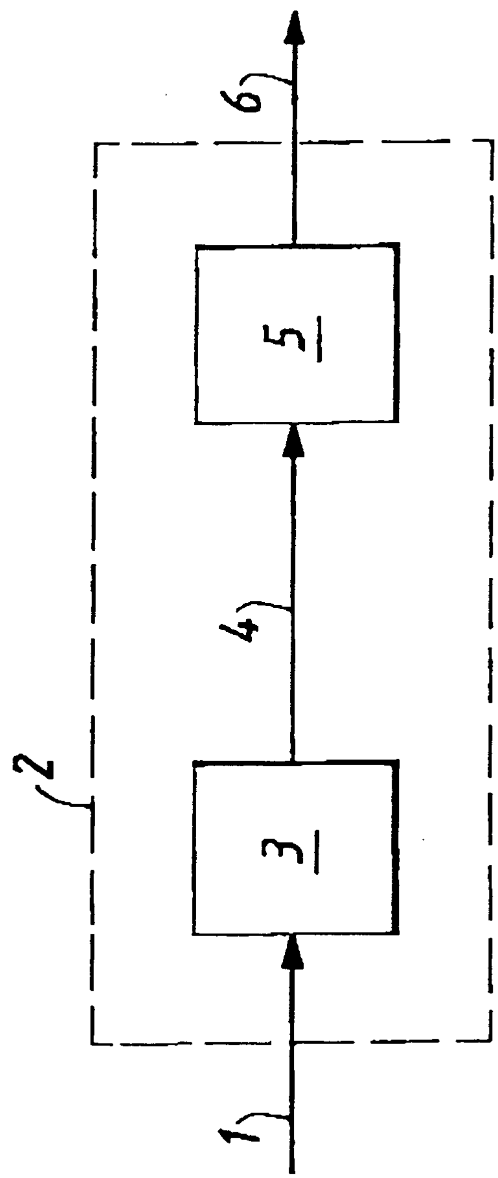

FIG. 3.

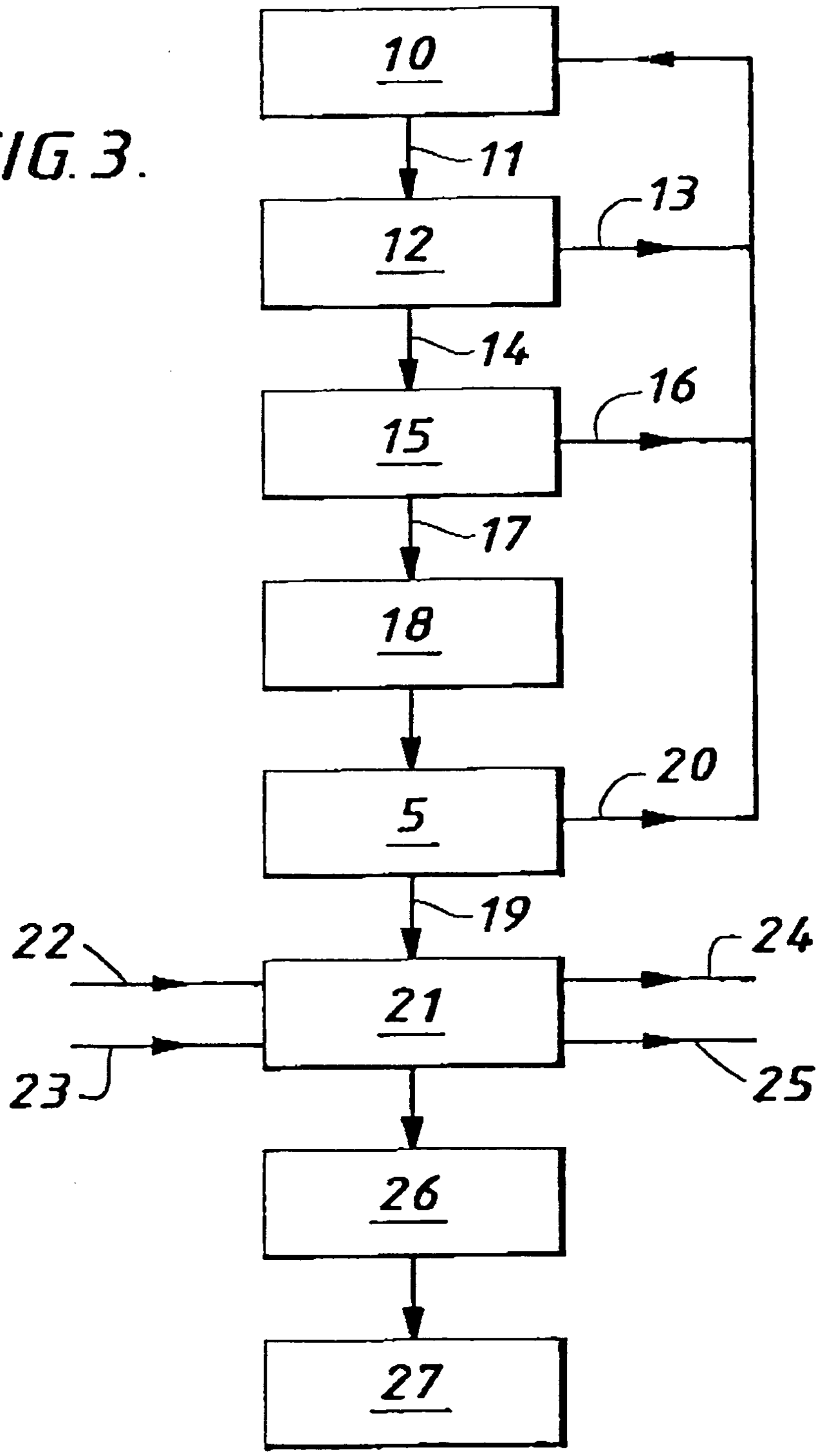

FIG. 4.

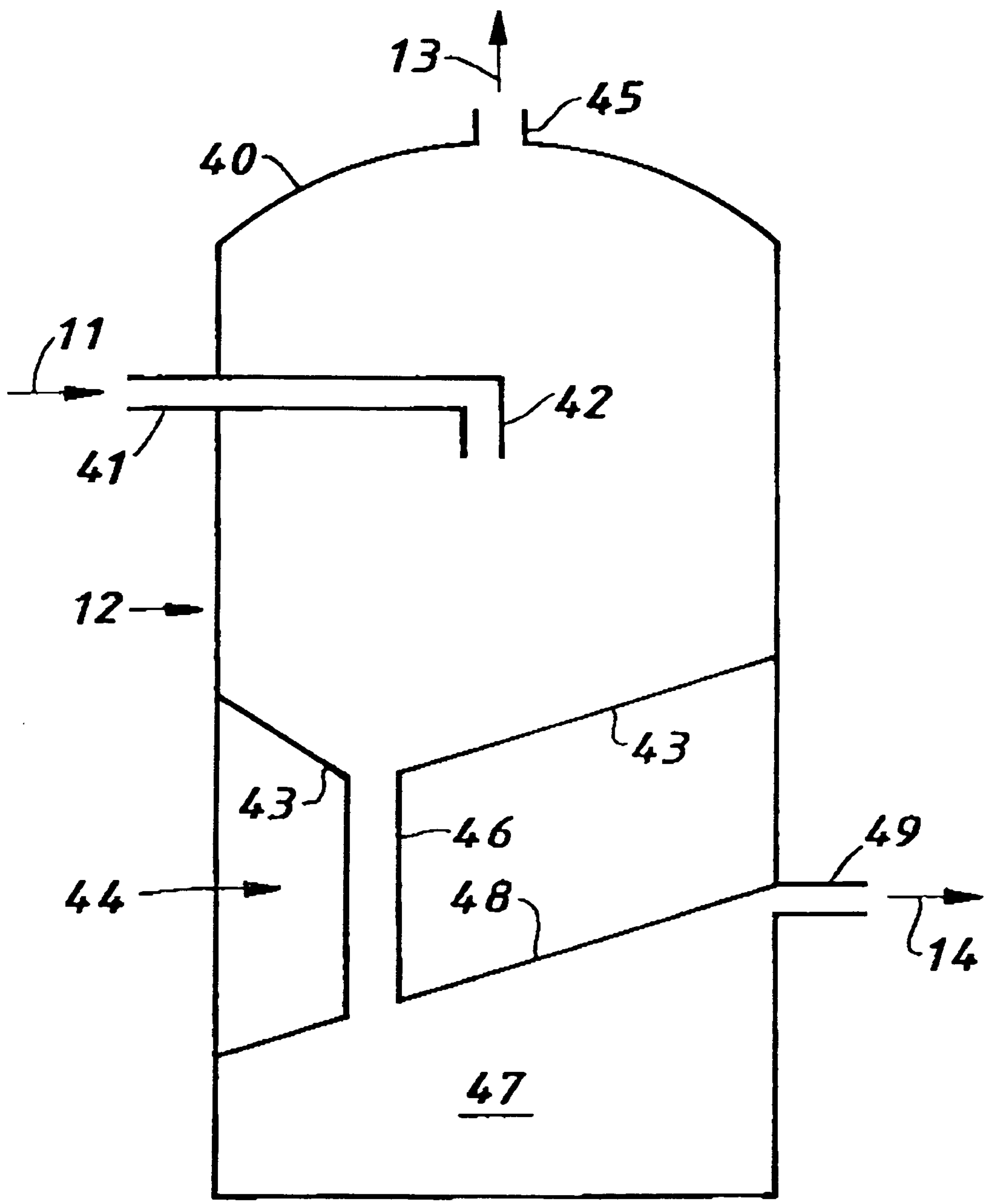

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FIG. 5.

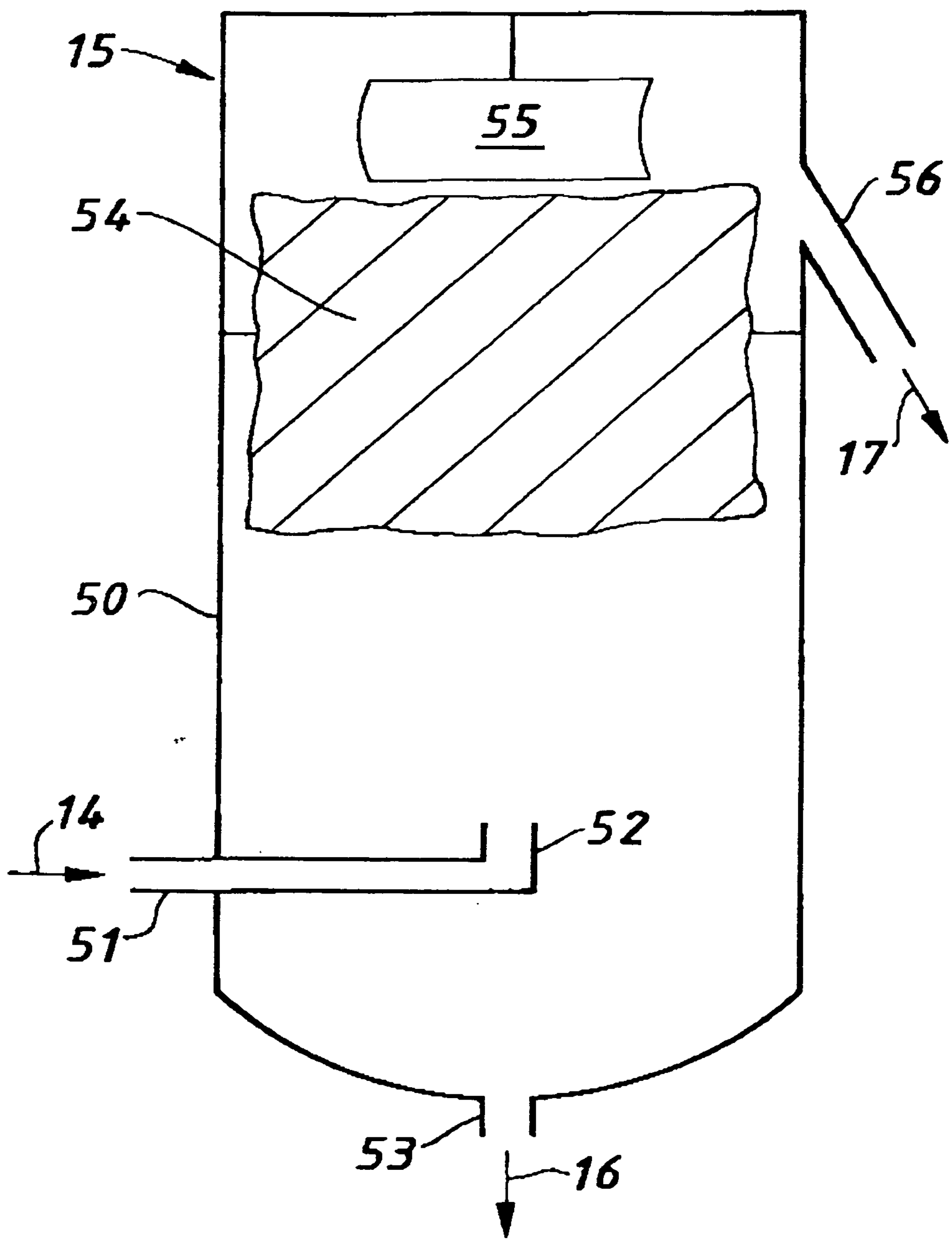


FIG. 6.

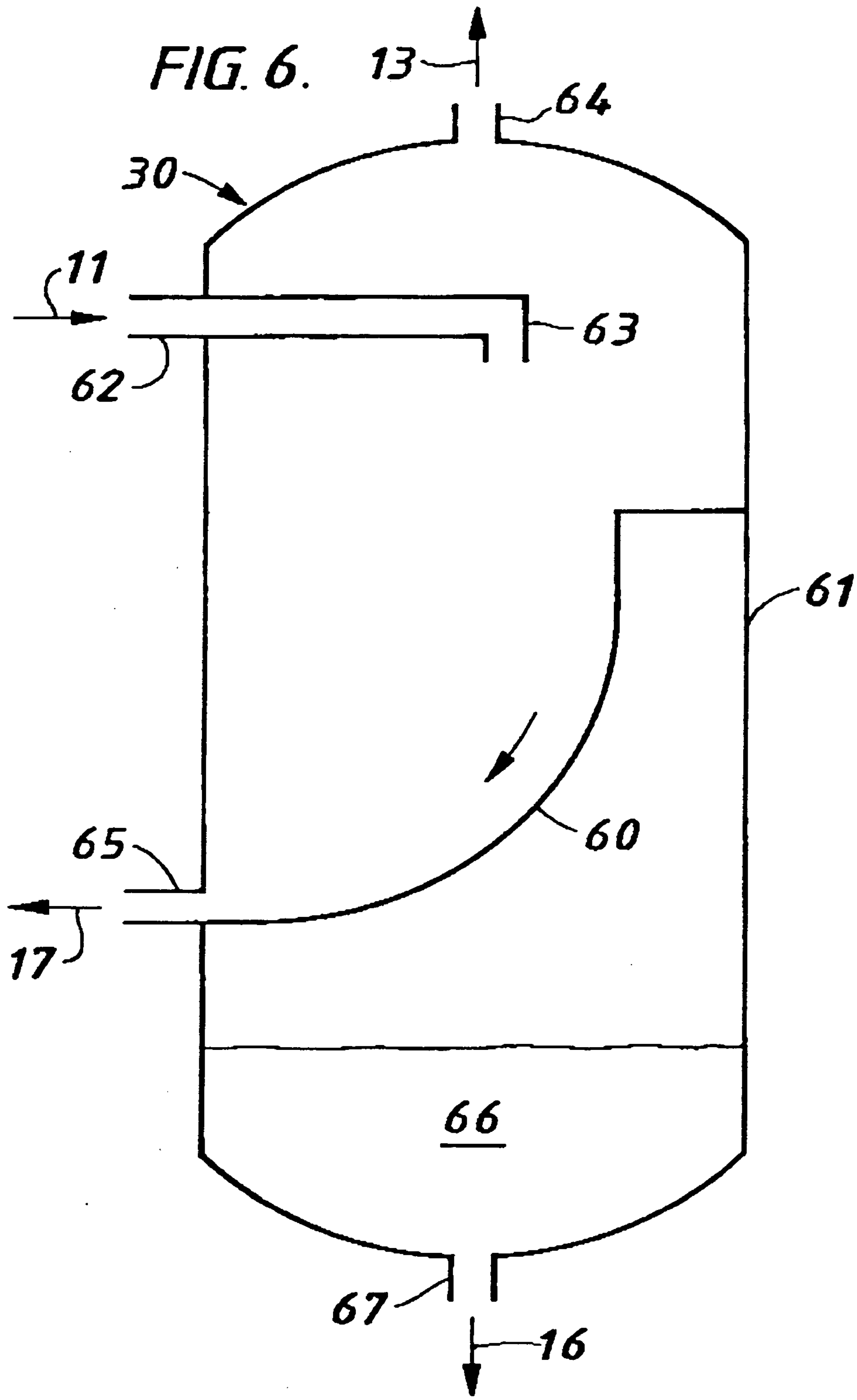
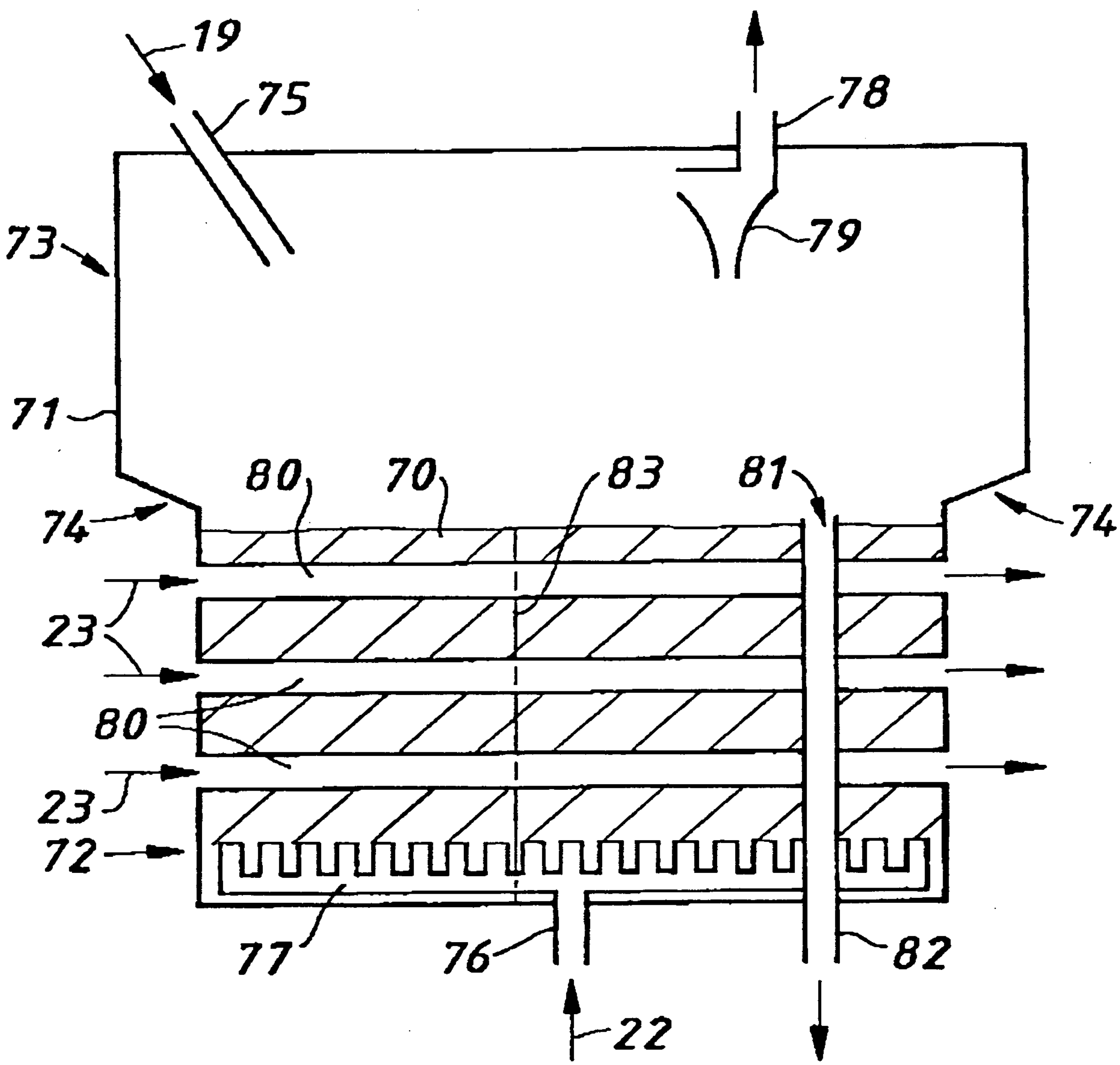
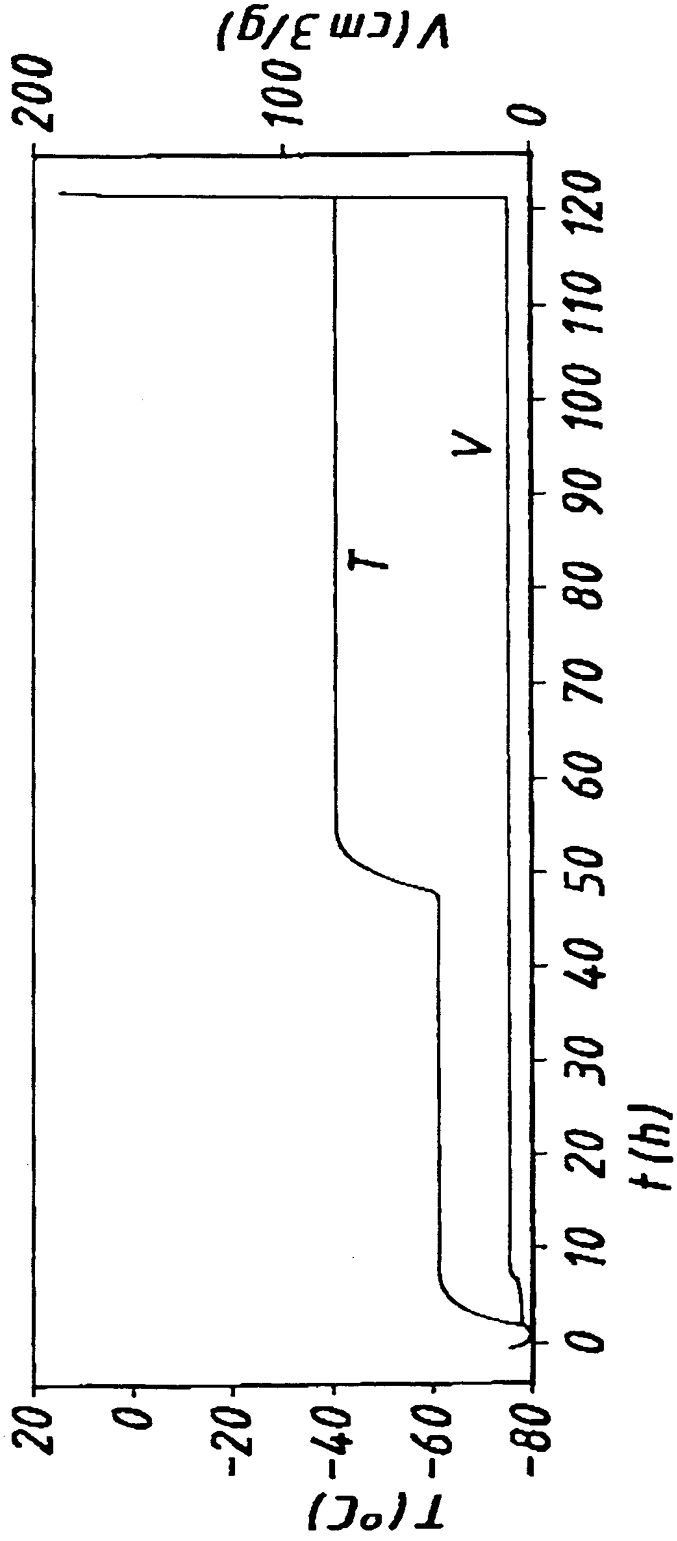


FIG. 7.

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0
T
V
20
0
-20
-40
-60
-80
T(oC)
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10
20
30
40
50
60
70
80
90
100
110
120
t(h)

FIG. 8.

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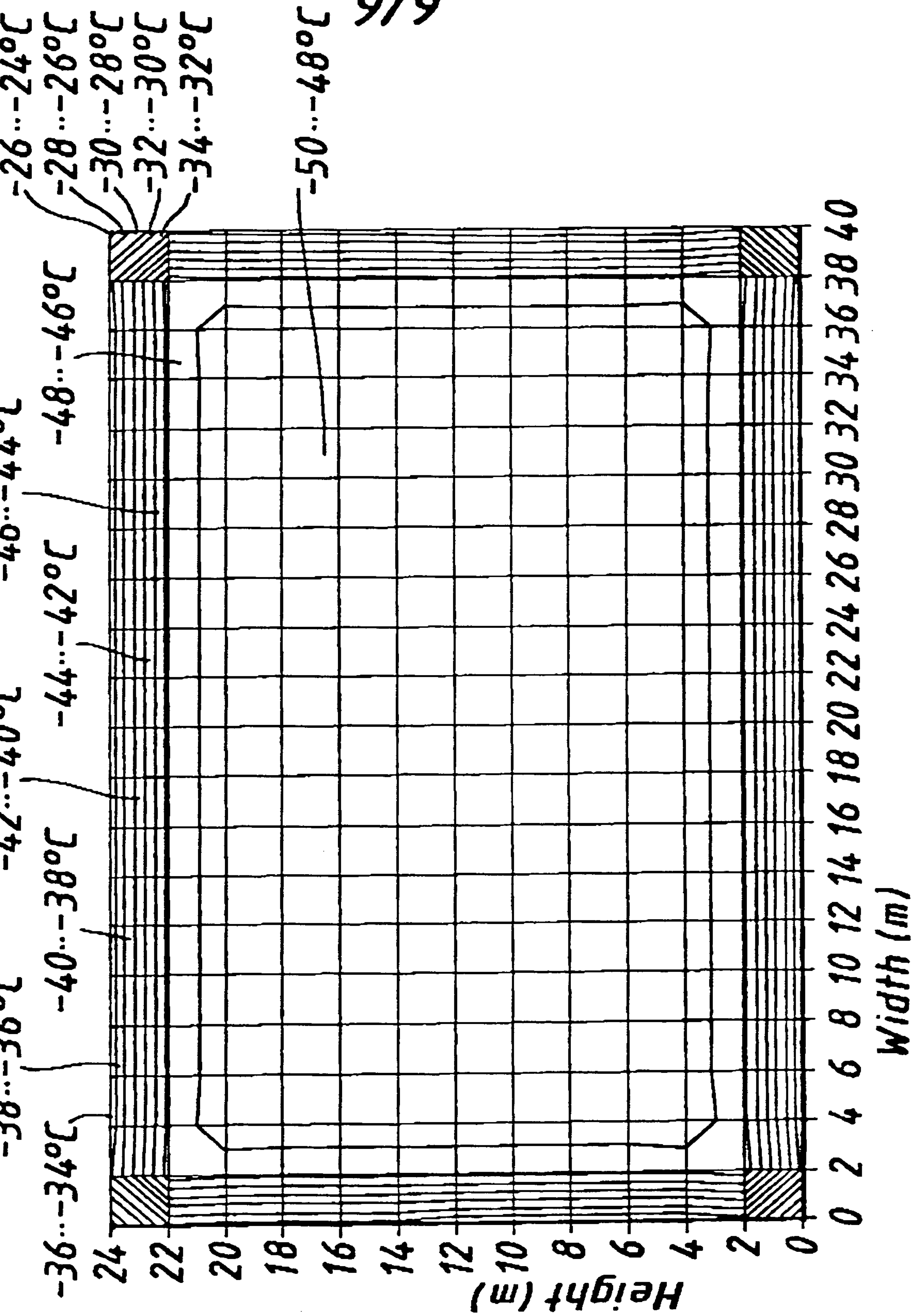
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-28...-26°C
-30...-28°C
-32...-30°C
-34...-32°C
-50...-48°C
-48...-46°C
-46...-44°C
-44...-42°C
-42...-40°C
-40...-38°C
-38...-36°C
-36...-34°C
Height (m)
24 22 20 18 16 14 12 10 8 6 4 2 0
Width (m)
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40

FIG. 9.

PCT/ GB 00 / 00 9 42

15 - 3 - 00

B 9 PLC